



## MANUFACTURING OF TWO STEP CONTINUOUS OF UP-SCALED SOY-POLYURETHANE

Flora Elvistia Firdaus

Department of Chemical Engineering, Jayabaya University, Indonesia

E-Mail: [flora\\_elvistia@yahoo.com](mailto:flora_elvistia@yahoo.com)

### ABSTRACT

The tryglyceride of vegetable oils should have at least one of unsaturated fatty acid moiety to be modified with sulfur acid catalyst in peracetic acid co-reagent, to be introduced to the desired hydroxyl functional groups in soy-polyol structure. A series of screening reactions have indicated the ratio of acetic/peroxide acid 1:7.25 (mol/mol) with temperature 60°C is the best condition for soy-epoxide to be up-scaled to 10 and 20 folds from initials. A 90 minutes is the best length of reaction for polyol to be synthesized where the oxirane value and acid value occurred are quite preferable for the proceed reactions. The recommended reactor volume is multiple of 400 mL. There are tendency of increasing the acid number if the volume enlarged 10 times, so it needs repeated neutralizations. New methods are need for the cost efficient.

**Keywords:** acid number, polyurethane, soy polyol, two step continuous, up-scale.

### INTRODUCTION

Vegetable oils are sustainable resources and the most established and abundance feedstock for chemical industry with steady in demand. Soybean oil as one among vegetable oils contains carbon-carbon double bonds in its fatty acid chain with no hydroxyl groups. Several processes used to introduce hydroxyl groups into the carbon-carbon double bond like epoxidation reaction or addition of oxygen reaction forming oxirane rings. The unreacted hydroxyl groups are account as reactive site of polyols which then act as intermediates in the formation for industrial fatty acid derivatives (Goud VV. *Et al*, 2006); (Biermann, U. *et al.*, 2000). Higher residual acidity is an undesirable polyol property as it competes with hydroxyls to react with isocyanates and consumes catalyst when is furthered processed to produced polyurethane.

#### Reactive sites of tryglycerides to modified

Soybean oil has 85% of unsaturated fatty acid chains, the reactivity of fatty acid is depend on the amount of carbon double bond, three carbon-carbon  $\pi$ -bond of linolenic acids which are more reactive to be polymerized by oxidation than linoleic (18:2) and oleic (18:1) (Li F. Larock, R.C, 2001; Li F. Larock, R.C., 2000; Erhan, S; sheng, Q., Hwang H.S., 2003).

Epoxidized soy-oil (ESO) is one of raw material used in synthesizing foams of flexible polyurethane; the double bond of soybean oils are the focus target with the multiples hydroxyl. Several methods has been used for epoxides ring opening which have resulted many different polyols, where are ready to be converted to different polyurethane characteristics (A. Guo, Cho Y., Petrovic Z.S., 2000).

Soy-based polyol retains the triglyceride backbone with hydroxyl functionality for addition reaction to increase the isocyanates reactivity. A 100% conversion

of oxirane group to hydroxyls was occurred by oxiranes dangling in central position of fatty acid chain. The short carbon chain before and after the hydroxyl group acted as plasticizer and improved polyurethane properties which then reduce the rigidity (Fedderly, Lee J.J., 2000). Oxirane ring opening reaction are effective for converting soybean oil to secondary moieties polyols but react slower than primary moieties which requires lower catalyst quantities (R. Herrington, K.Hock, 1997). Polyols from vegetable oils also known as biopolyols, performed as main substances of intermediates for polyurethane production. The hydroxyl values in polyols are related to this research design and methods.

#### The effectiveness of co-reagent for proceed reaction

Ethylene glycol is an effective co-reagent for soy epoxidised alcoholysis reaction. The increase reactivity of epoxide to ethylene glycol was attributed to the primary hydroxyl functionality (Zuleica L. Rodriguez, 2009; Flora, Firdaus E, 2014).

### METHODOLOGY AND MATERIALS

Soybean oil was purchased from local grocery, acetic acid, peroxide acid, ethanol 96% with the used of sulfur acid catalyst. The reaction was conducted in designated temperatures; at 60°C and for ring opening was at 117°C. The products obtained from epoxidation reaction was neutralized, decanted, and filtered. The ingredients of soybean oils transformation to epoxides was a blending of acetic acid and peroxide (peracetic), in the compositions ratio of acetic/peroxide (1:7.25) (mol/mol) was labelled as A; (1:7.255) (mol/mol) as B, and (1: 7.8) (mol/mol) as C. The optimized conditions of laboratory scale of soy-epoxide are prevail to the up-scaling into 10 and 20 folds from initials. Polyurethane was made by mixing polyols,



TDI: MDI (80:20), surfactants, and blowing agent; a distilled water.

## EXPERIMENTAL SET UP

### Screening study

Screening studies was conducted to evaluate conditions to the effectiveness of soybean oil epoxidation. These conditions are; temperature, amount of catalyst, amount of peroxide, and amount of acetic acid. For the screening study, 100 mL of soybean oil was charged with peracetic acid in fixed formula using concentration of sulfur acid 1%; 2%; and 3% (v/v) as catalyst, with temperature at 60°C. Oxiranes numbers are values of measuring the unsaturated fatty acid which has transformed and forming oxiranes ring.

The best oxirane number occurred for the designated sulfur acid concentration at 1% (v/v) was 6.7%, at 2% (v/v) was 7.3% and the best oxirane number at 3% (v/v) was 3.9% and 4.5%. However for the proceeds reaction for the catalysis purposes, the amount of catalyst used was 1% (v/v).

### Epoxidation reaction

Soybean oil (400 mL) and acetic acid were added into the 500 mL round bottom flask which equipped with a thermometer, and mechanical stirrer. The hydrogen peroxide was added slowly to this mixture. The temperature was maintained at 60±0.5°C.

The slow addition of hydrogen peroxide was performed to prevent overheating of the exothermic reaction occurred during reaction.

The ratios of acetic/peroxide acid were designed in three forms: (1:7.25); (1:7.255) and (1:7.8) (mol/mol) as respectively was named as A, B, and C. The volume of bodied soybean oil was designed in laboratory scale for A: 400 mL was named as A-400 and up-scaled to 1200, 2400, and 4000 was named as AA-1200, AA-2400, and AA-4000. The second was B, the volume of bodied soybean oil was made in 400 mL was named as B-400 and the volume of up-scale was made in 800 mL and 1600 mL was named as B-800 and B-1600. The third was C, it was named as C-600 with no up-scale this is was set up as control variable. The concentrations were summarized in Table-1.

**Table-1.** The concentration at laboratory and up-scale of peracetic ratio for epoxidation.

Foam Code	Initial Volume	Up-Scaling
A	A-400	AA-1200
		AA-2400
		AA-4000
B	B-400	B-600
		B-1600
C	C-600	ND

Peracetic ratio A (1:7.25); B(1:7.255); and C (1:7.8) (mol/mol)

Epoxy content of the samples and the acid number of of all products were measured and evaluated by AOCS official method (AOCS, 1997).

The samples were analysed using FTIR to qualitatively follow the disappearance of double bonds and formation of oxirane ring.

### Hydroxylation reaction

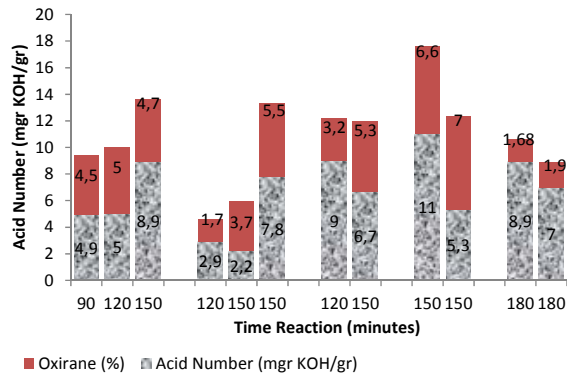
The hydroxylation reaction is the ring opening reaction of epoxide by ethylene glycol. The ethylene glycol is made in fixed ratio 1:0.19 (mol/mol), the volume of epoxide was made in eight; (50); (100); (300); (500); (700); (1000); (1000), and (2000) mL. The hydroxyl number, reduction of oxirane number, and the scale-up of epoxide were observed to know the consistency properties from laboratory to up-scale.

Hydroxyl values of polyols were determined according to ASTM Procedure (ASTM, 2005).

## RESULTS and DISCUSSIONS

### Synthesis of polyol

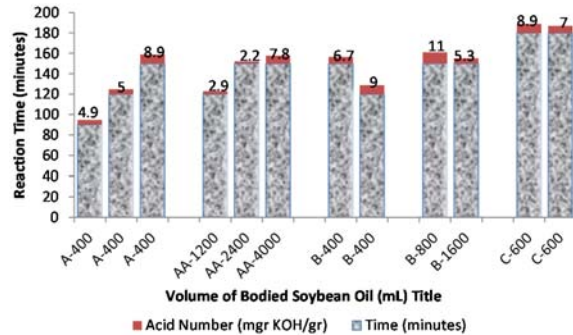
The epoxide occurred from soybean oil epoxidation by variations of time reaction which are: 90, 120, 150, and 180 minutes at varied ratio peracetic 1:7.25; 1:7.255; and 1:7.8 (mol/mol). The time reaction at 150 minutes has resulted the best oxirane number among other designated time reactions which are above 4 mgr KOH/gr. Time reaction either below or above 150 minutes at averages are below 4 mgr KOH/gr. The oxirane value indicates the degree of epoxidation that has occurred, which understood can influenced physical properties of polyurethane, because the -OH formation from alcoholysis of epoxide are performed as reactive sites to isocyanates, which performed as soft domain in polyurethanes.



**Figure-1.** Effect of time reaction to acid number and oxirane number on epoxide synthesis.

The acid number is increased eventhough undertaken by fixed ratio of epoxide/ethylene glycol, and at fixed temperature  $60\pm 0.5^{\circ}\text{C}$  it is a matter of time reaction where epoxide and ethylene glycol were contacted longer. In this study the epoxides occurred were meant to be neutralized in once as to know the acid content remain. As can be seen in Figure-1.

During the hydroxylation reaction, the acidity of polyol was made from ratio of peracetic acid 1:7.25 (mol/mol) in 400 mL volume of soybean oil was 4.9 mgr KOH/gr in 90 minutes reaction which gradually increased to 5 mgr KOH/gr to 8.9 mgr KOH/gr sample at 120 minutes and 150 minutes. The up-scaling to volume 1200 mL for time reaction 120 minutes, the acid number was declined to 2.9%. If the volume doubled to 2400 mL for time reaction 150 minutes the oxirane was continue lowering to 2.2 mgr KOH/gr eventhough still at same length of reaction (150 minutes). But if the volume were enlarged to 4000 mL the acid number again risen to 7.8%. For ratio 1:7.255 (mol/mol) with volume of soybean oil 400 mL for 120 minutes was 9 mgr KOH/gr sample but were declined in 150 minutes to 6.7 mgr KOH/gr. Low acidity in epoxide either is important which is preferable under 10 mgr KOH/gr (Monteavaro, 2005). The brief result were drawn in Figure-2.



**Figure-2.** Acid number volume of bodied soy-bean, ratio of acetic to peroxide acid to reaction time at fixed temperature at  $60\pm 0.5^{\circ}\text{C}$ .

The formation of epoxide, certain side reaction can occurred, and decomposition of peroxy acid. The multiple sites of unsaturation per tryglycerides and per fatty acid chain in vegetable oils which makes the result with peroxy acids does not directly to the formation of fully epoxidised oil but also formation of partially epoxidised precursors.

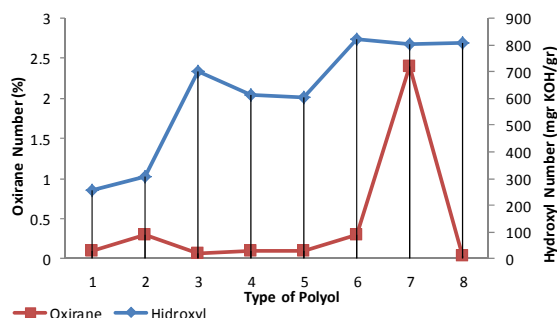
As the volume doubled to 800 mL with reaction time 150 minutes has declined of oxirane number to 5.3 mgr KOH/gr which previously was analysed because the unhomegenized mixing process, but this analysis were prematurely fall as up-scaled to 1600 mL followed by risen of oxirane to 11 mgr KOH/gr sample. The acid number was found high at concentration 1:7.8 (mol/mol) is 7 mgr KOH/gr sample and 8.9 mgr KOH/gr sample in 150 minutes for 600 mL.

The acid number and oxirane number is a function of time and temperature. The acid number at 5.3 mgr KOH/gr sample has reached the highest oxirane number it was 7 %. The value of acid number below and above 5.3 mgr KOH/gr sample. The low acidity in polyol is still preferable because high acid valued in polyols tend to neutralize the urethane formulation catalyst. The oligomer polyol product may have light yellow to dark brown yellow. The increased of acid number could be due to the degradation of as a result of the reaction over 150-180 minutes, even the reaction was at fixed temperature. But the time reaction predominantly effected to hydroxylation reaction of epoxide which assume was completed and the product occurred has oxirane number as a function of time of which was increase.

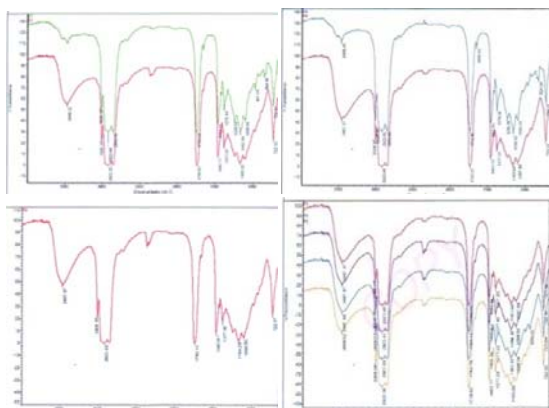
The steady increase in hydroxyl number may attribute to continued breaking of ester bond. Ethylene glycol to epoxide was made in fixed ratio which was 1: 0.19 (mol/mol) and in fact the volume of epoxide was 10 and 20 folds from initials which have reached the optimum condition and the high value of hydroxyl number of polyol. The crosslinking performance correlates to hydroxyl values of soy-based polyols, achieved from



bodying the partially epoxidized functional groups and ethylene glycol addition which had caused to increasing alcohol functional groups. The bodying of soy-based epoxide was employed to control moieties and avoid reaction with hydroxyl groups. It seems the high amount of unreacted oil could not be avoided as we can see the value of acid number increase with a function of time.



**Figure-3.** Hydroxyl number related to oxirane number of polyol at fixed ratio of ethylene glycol/epoxide (1:0.19) (mol/mol).



**Figure-4.** FTIR of soy-epoxide and soy-polyol.

The FTIR spectra of soy-base epoxide, the disappearance of epoxy groups at 825 and 845  $\text{cm}^{-1}$  the appearance of hydroxyls at 3450  $\text{cm}^{-1}$  are clear. The final product of soy-based polyol shows the characteristic signal at 1050  $\text{cm}^{-1}$  which showed the existence of esters group.

## CONCLUSIONS

The acid number and oxirane number are correlates to the time and temperature function. The steady temperature with increment time reaction will degrade oil and resulted the high acid number. The steady increase of hydroxyl number may attributed to continued breaking of ester bond. The upscaling from the bench scale does not gives the significantly different in physical properties.

## ACKNOWLEDGEMENT

The author gratefully acknowledge the support of the Indonesia Department of higher education as funding the research.

## REFERENCES

- [1] Goud VV, Patwardhan AV, Pradhan NC. 2006. Studes on the epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide. *Bioresource Technol.* 97(12): 1365-1371.
- [2] Biermann U., Friedt W., Lang S., Luhs W., Machmuller G., Metzger J.O., Klaas M.R., Schafer H.J., Schneider M.P. 2000. New synthesis with oils and fats as renewable raw materials for the chemical industry *Angew. Chem. Int. Ed.* 39: 2206-2224.
- [3] Li F. Larock, R.C. 2001. New soybean oil-styrene divinylbenzene thermosetting copolymers I Synthesis and characterization. *Journal of Applied polymer science.* 80(4): 658-670.
- [4] Li F. Larock, R.C. 2000. New soybean oil-styrene divinylbenzene thermosetting copolymers II. Dnamic mechanical properties. *Journal of polymer science Part B: Polymer physics.* 38(21): 2721-2738.
- [5] Erhan S, sheng Q. 2003. Hwang H.S., Volatile products during polymerization of soybean oil. *Journal of the American oil chemists' Society.* 80(2): 177-180.
- [6] Guo A, Cho Y, Petrovic ZS. 2000. Structure and properties of halogenated and non halogenated soy-based polyols, *J. Polym Sci [A].* 38: 3900-3910
- [7] Fedderly, Lee JJ, Lee GF, Hartmann JD, Dusek B, Duskova Smrckova K, Somvarsky M. 2000. Network structure dependence of volume and glass transition temperature. *The Soc Rheol Inc J Rheol.* 44: 961-972.
- [8] R. Herrington, K. Hock. 1997. Flexible foams. The Dow chemical company, midland, MI.
- [9] Zuleica L. Rodriguez. 2009. Chemical modifications to produce soy-based polyols, Dissertation, University of Missouri Columbia. p. 39.
- [10] Flora Firdaus E. The Selection reaction of Homogeneous Catalyst in Soy-Epoxide Hydroxylation. *Journal of Physics: Conference Series.*



Vol. 495, 2014 IOP Science doi: 10.1088/1742-6596/495/1/012013) SCOPUS.

- [11] Flora Firdaus E. 2014. Synergization of Silicone with Developed Crosslinking to Soy-Based Polyurethane Foam Matrix. International Conference on Manufacturing, Optimization, Industrial and Material Engineering, Jakarta, 29-30 March (proceeding), pp. 176-182.
- [12] AOCS. 1997. Official Methods and recommended practices of the American oil chemists' acid value, AOCS Te 1a-64, Champaign, IL.
- [13] AOCS. 1997. Official Methods and recommended practices of the American oil chemist's society, oxirane oxygen in epoxidized materials, AOCS Cd 9-57, Champaign, IL.
- [14] 2005. American Society for testing materials. Polyurethane raw materials: determination of hydroxyl numbers of polyold, Designation: procedure E222-00 Method A: West Conshohocken, PA.
- [15] L.L. Monteavaro, E.O. Da Silva, A.P.O, Costa, D.Samios, A.E. Gerbase, C.L. Petzhold. 2005. J. Am. Oil Chemist's Soc. JAOCS), 82/5: 365.